

Mercury Analysis in Fish Matrix

Sanwat N. Chaudhuri, Ph.D., Steven J. M. Butala, Ph.D.* , and
Larry P. Scanlan

Utah State Public Health Laboratories

in collaboration with

Utah DEQ/ Division of Water Quality

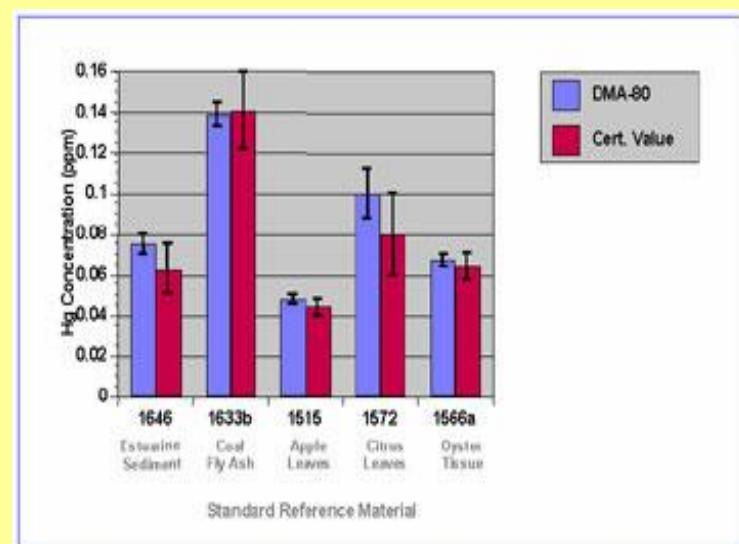
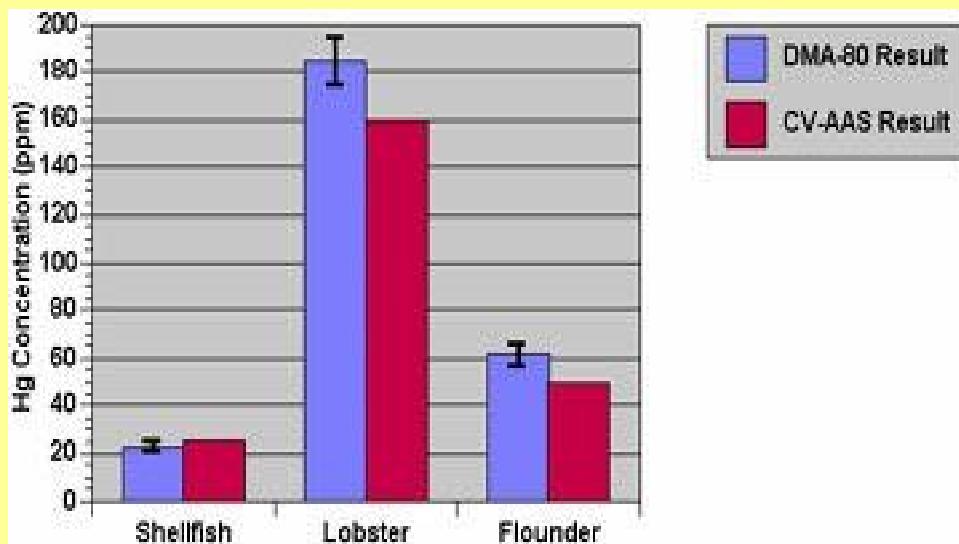
February 08, 2006, Mercury Workgroup Meeting
Salt Lake City, Utah

Background

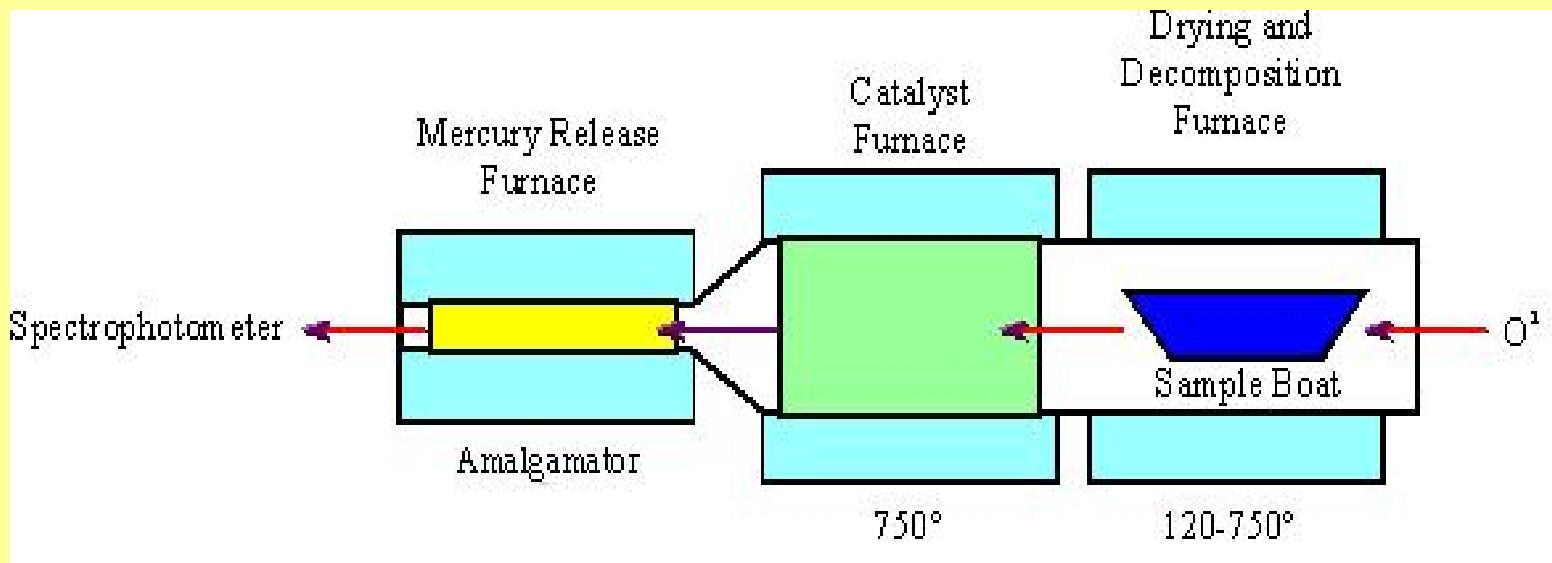
- Request from DEQ/DWQ
- Research methods
- Instrument funded by DWQ
- Method validation
- Quality Assurance/Control
- Sample analysis

Methods Research

- EPA 7473
- Comparison with AA and ICP/MS
 - Literature reports either comparable or slightly biased high results



Theory: Direct Mercury Analyzer



Direct Mercury Analyzer



Direct Mercury Analyzer



Method Goals

- High accuracy
- High precision
- High Quality Assurance
- High-throughput (50 samples/week in duplicate)
- Three-week time constraint

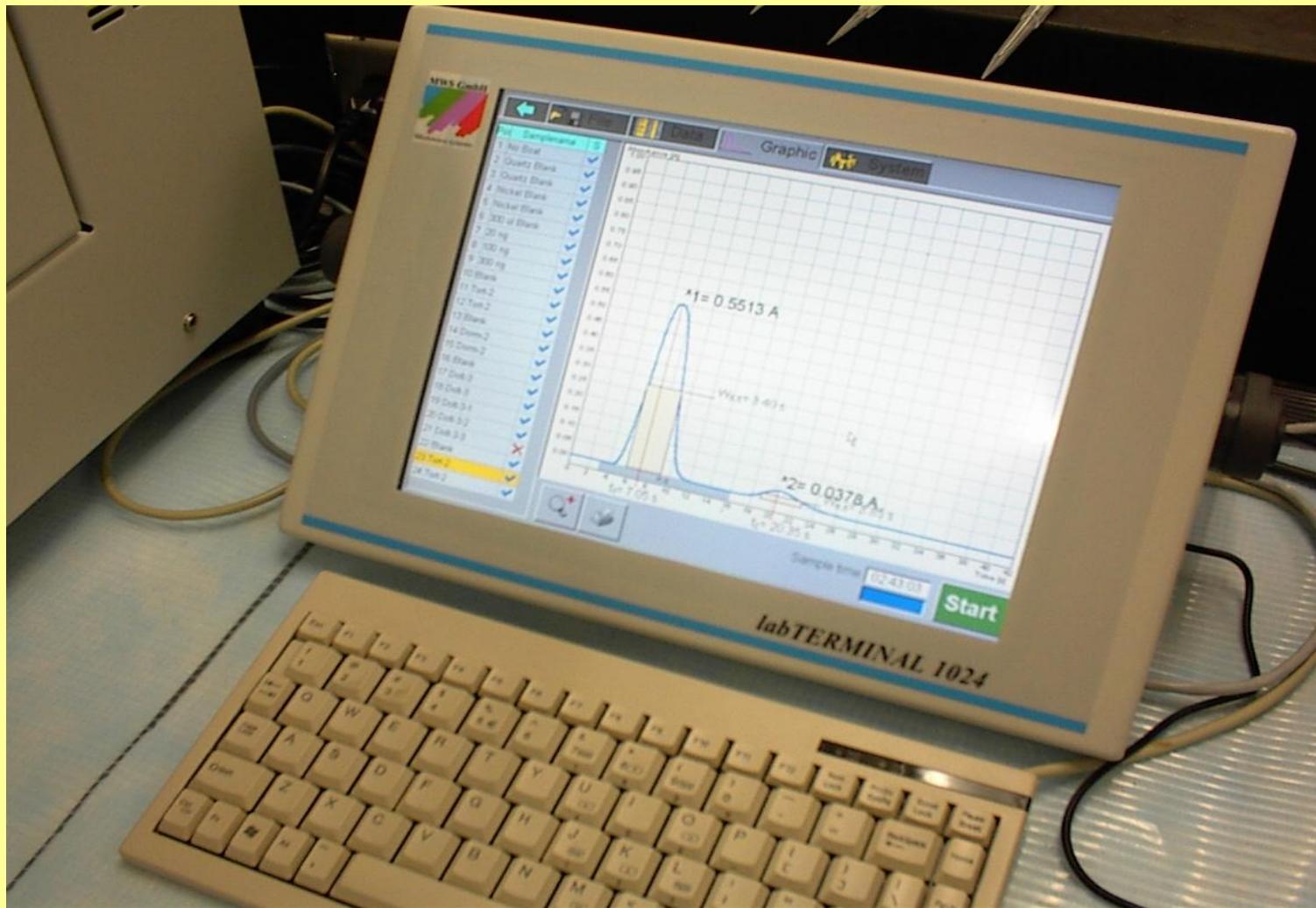
Method Validation

- Measured Values
 - IDL = 0.01 ng
 - MDL = 0.0017 mg/kg
 - 10 replicates of salmon fillet
 - MRL = 0.030 mg/kg*
- Literature Values
 - IDL = 0.01 & 0.02 ng
 - MDL = 0.0009 mg/kg
 - 8 replicates of tilapia homogenate
 - MRL = ***

Screening Value (SV) = 0.3 mg/kg

* Practical quantitation value

Assuring Quality Measurements



Calibration Curves were Carefully Analyzed and Modeled, Statistically

Regression Analysis for Cell #1: Height versus X, X^2, X^3

The regression equation is
 $\text{Height} = 0.0322 \text{ X} + 0.000089 \text{ X}^2 - 0.000007 \text{ X}^3$

Predictor	Coef	SE Coef	T	P
Noconstant				
X	0.0321710	0.0002501	128.64	0.000
X^2	0.0000895	0.00003038	2.93	0.015
X^3	-0.00000662	0.00000086	-7.70	0.000

S = 0.001483

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	3	2.43698	0.81233	369260.56	0.000
Residual Error	10	0.00002	0.000000		
Total	13	2.43700			

Source	DF	Seq SS
X	1	2.43518
X^2	1	0.00167
X^3	1	0.00013

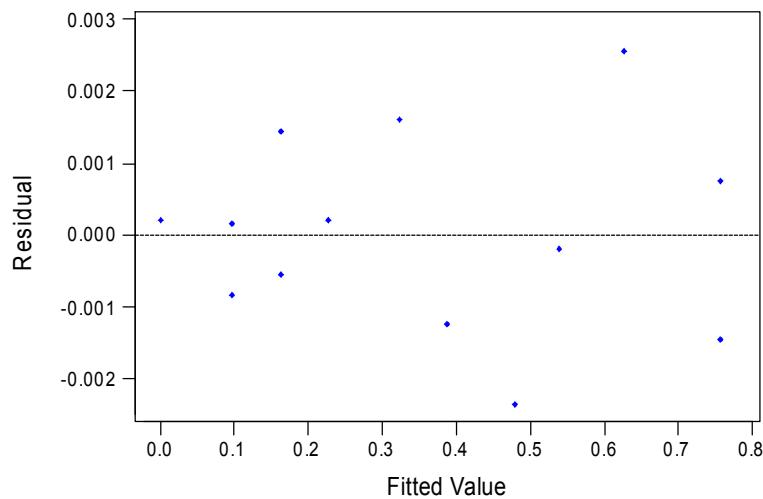
Unusual Observations

Obs	X	Height	Fit	SE Fit	Residual	St Resid
11	20.0	0.628600	0.626053	0.000830	0.002547	2.07R

R denotes an observation with a large standardized residual

Residuals for Cell #1 Versus the Fitted Values

(response is Height)



Quality Assurance

- Standard curve ($R^2=0.9999$)
0.003 µg - 0.4 µg
0.042 mg/kg - 5.7 mg/kg
- Instrument blank
- Wash blank every 10 samples
- Homogenize sample
- All analysis in duplicate
- SRM in every 10 samples
- SRMs at two levels
- Round Robin
- PT
- Duplicate criteria
 - <0.02 mg/kg = 20% RSD
 - 0.02 - 0.2 mg/kg = 15%
 - 0.2 - 0.4 mg/kg = 10%
 - >0.4 mg/kg = 5%
- Re-analyze outside criteria
- SRM criteria (manufacturer)
 - 0.2 - 0.3 mg/kg = 22% rpd
 - >0.4 mg/kg = 11% rpd
- EPA Method 7473
~20% RPD

Quality Assurance continued

- Reduction of all Contamination Sources
 - Teflon[®] vs. polypropylene
 - High purity acid and high purity water ($18\text{ M}\Omega$)
 - Blades, forceps, cutting board, bottles, tubes
 - Cutting board cleaned in acid bath
 - Pre-screen sample containers for Hg
 - Board and tools washed with hexane in between samples.

Quality Assurance continued

Analytical Performance of Quality Assurance Samples (SRM)

Replicate 1 (mg/kg)	Replicate 2 (mg/kg)	Mean (mg/kg)	Std. Dev.	%RSD
0.3080	0.3070	0.3075	0.0007	0.23%
0.3001	0.3031	0.3016	0.0021	0.70%
0.3038	0.3046	0.3042	0.0006	0.19%

95% Confidence Interval for True Mean Value (Certified Value)

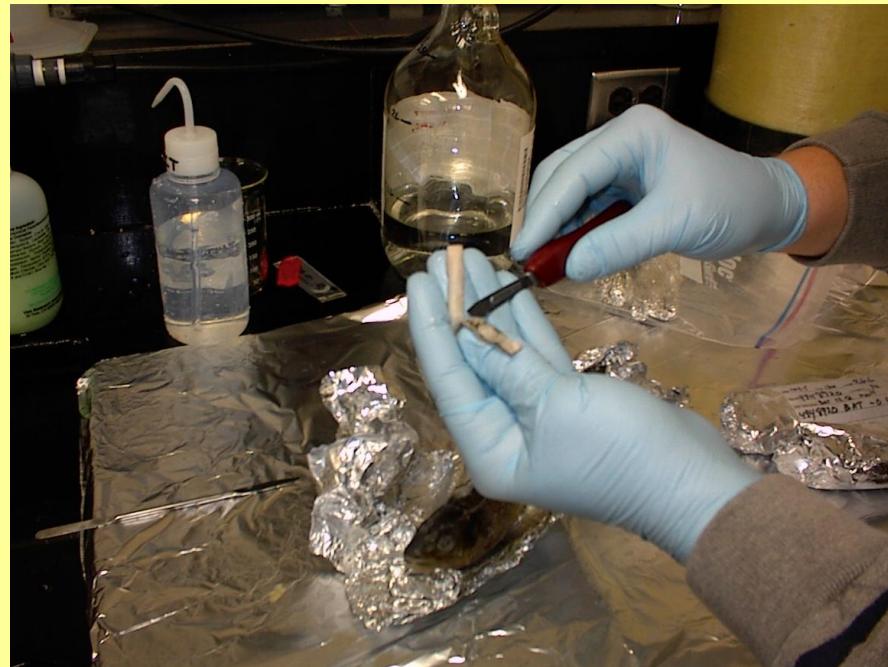
0.210-0.330 mg/kg

Sample analysis

- Sample collection
- Sample preparation
- Instrumental analysis
- Evaluation of data

Sample Collection and Preparation via Plug

- Plug
 - upper end of plug
 - lower end of plug



Sample results (plug) - Lake Powell

• Replicate 1 • ($\mu\text{g}/\text{kg}$) • 301.9*	• Replicate 2 • ($\mu\text{g}/\text{kg}$) • 295.1*	• Mean • ($\mu\text{g}/\text{kg}$) • 298.5*	• Standard Deviation • 4.8	• % RSD • 1.62
• 85.4	• 83.7	• 84.5	• 1.1	• 1.35
• 76.0	• 75.5	• 75.8	• 0.4	• 0.47
• 213.7	• 178.7	• 196.2	• 24.8	• 12.65
• 95.4	• 90.7	• 93.0	• 3.3	• 3.57
• 129.6	• 137.9	• 133.7	• 5.9	• 4.41
• 296.4	• 289.5	• 292.9	• 4.9	• 1.66
• 300.3*	• 308.1*	• 304.2*	• 5.6	• 1.83
• 128.6	• 131.1	• 129.8	• 1.8	• 1.36
• 175.5	• 223.9	• 199.7	• 34.2	• 17.14
• 191.1	• 261.1	• 226.1	• 49.5	• 21.89
• 124.3	• 121.9	• 123.1	• 1.7	• 1.38
• 157.3	• 165.0	• 161.2	• 5.4	• 3.35
• 297.8*	• 295.9*	• 296.8*	• 1.4	• 0.46
• * Health advisory level : 0.3 mg/kg (300 $\mu\text{g}/\text{kg}$)				
• 16% of overall data fell outside of duplication criteria				

Sample Preparation via Homogenization



Sample results (Homogenized)

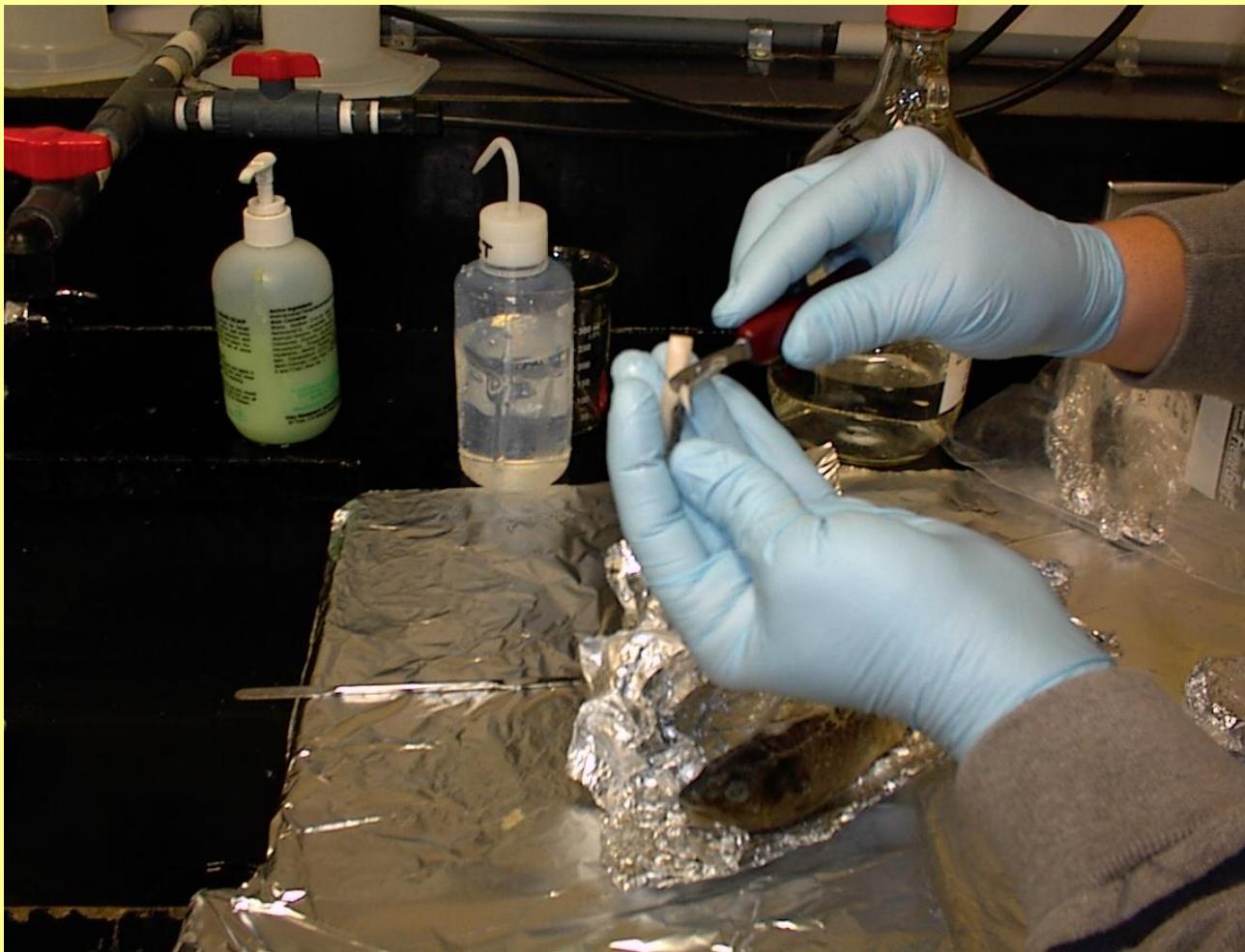
Sample#	data1 mg/kg	data2	mean	SD	RSD%
200600316	0.0723	0.0742	0.0733	0.0013	1.83
200600317	0.2545	0.2910	0.2728	0.0258	9.46* 6.7 rpd
200600318	0.0577	0.0601	0.0589	0.0017	2.88
200600319	0.0723	0.0723	0.0723	0.0000	0.00
200600320	0.0608	0.0684	0.0646	0.0054	8.32
200600321	0.0716	0.0655	0.0686	0.0043	6.29
200600322	0.2988	0.3278	0.3133	0.0205	6.55
200600323	0.0940	0.0983	0.0962	0.0030	3.16
200600324*	0.0004	0.0000	0.0002	0.0003	141.4*
200600325	0.1827	0.1904	0.1866	0.0054	2.92
200600326	0.5002	0.5037	0.5020	0.0025	0.49
200600327	0.2868	0.3056	0.2962	0.0133	4.49
200600328	0.0826	0.0794	0.0810	0.0023	2.79
200600329	0.0844	0.0844	0.0844	0.0000	0.00*
200600330	0.1165	0.1268	0.1217	0.0073	5.99
200600331	0.1820	0.1650	0.1735	0.0120	6.93
200600332*	0.0002	0.0001	0.0002	0.0001	47.14*
200600333	0.0774	0.0765	0.0770	0.0006	0.83
200600334	0.1216	0.1197	0.1207	0.0013	1.11
200600335	0.1229	0.1287	0.1258	0.0041	3.26
200600336	0.0694	0.0782	0.0738	0.0062	8.43
200600337	0.1749	0.1621	0.1685	0.0091	5.37
200600338	0.1617	0.2020	0.1819	0.0285	15.67*

Initial Sample Preparation and Check-In

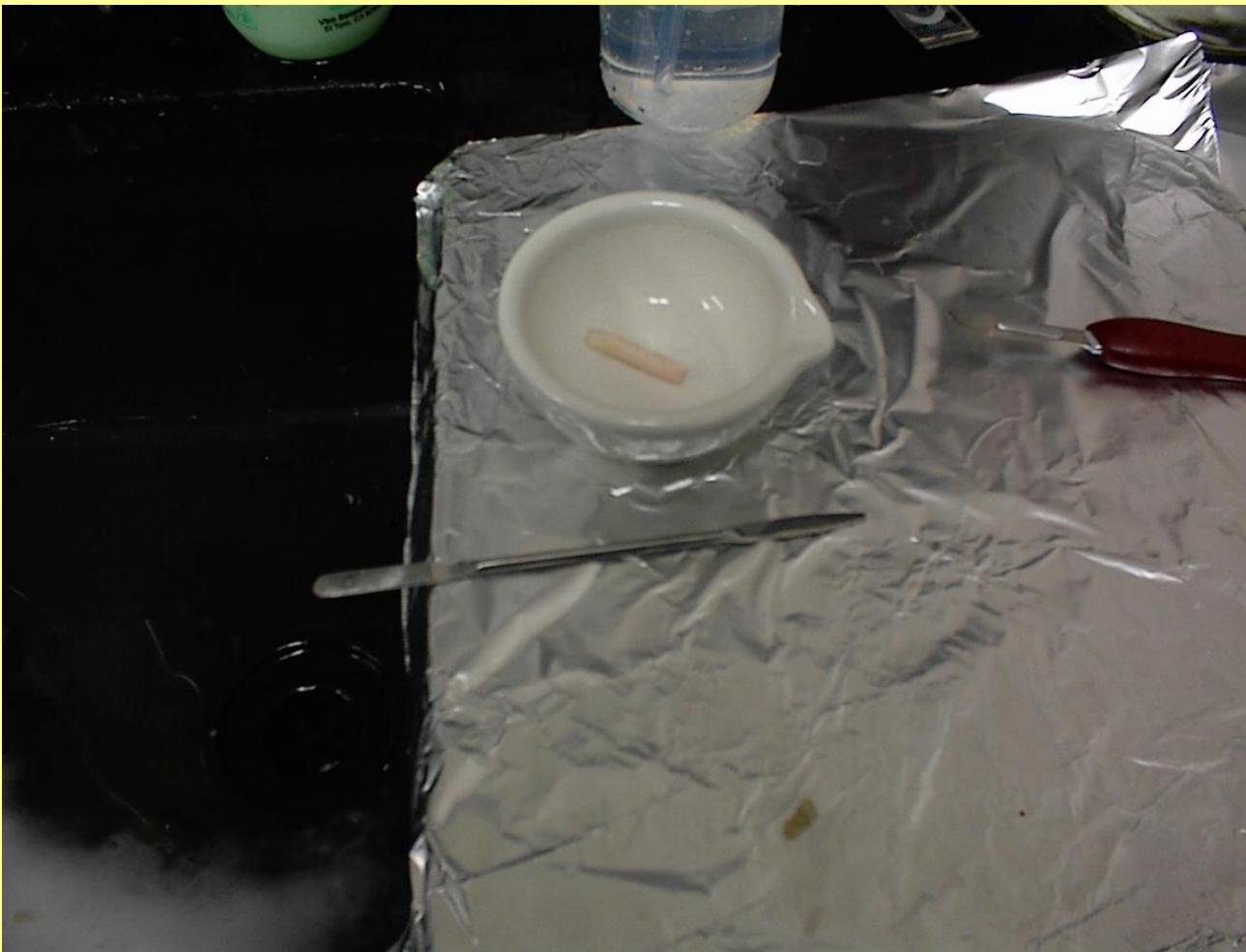
Sample Preparation-Plug Removal



Sample Preparation-Skin Removal



Sample Preparation-Plug Homogenization



Sample Preparation-Plug Homogenization



Sample Preparation-Cleaning



Checking for Carryover-Water Introduction



Checking for Carryover-Mixing of Water



Checking for Carryover-Removal of Water



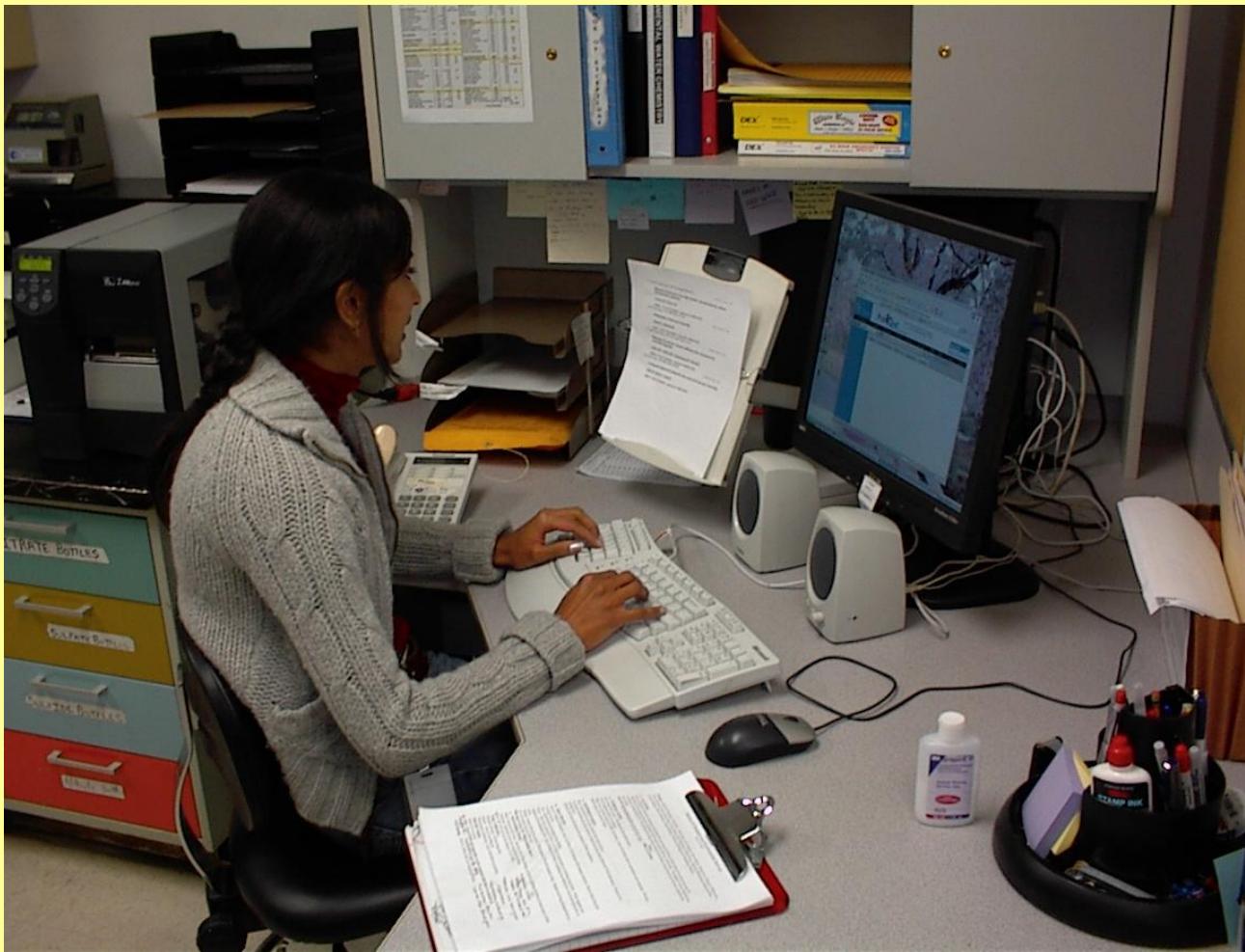
Checking for Carryover-Placing Water in Sample Tube



Checking for Carryover-Acidifying Carryover Water Sample



Prepared Samples being Checked-In



Temporary Freezer for Fish Samples



Permanent Freezer for Fish Samples



Permanent Freezer for Fish Samples



Final Sample Preparation and Analysis

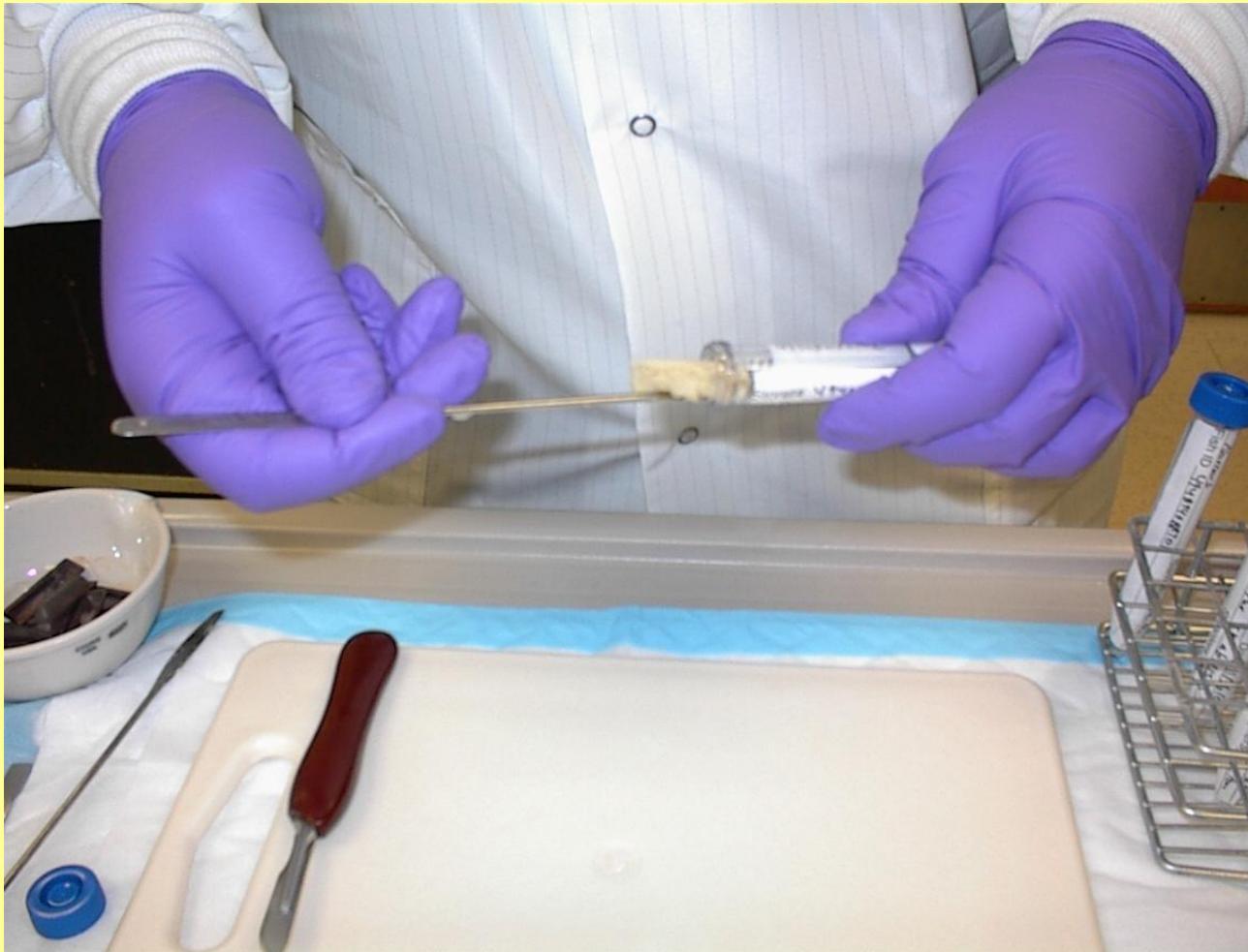
Cutting Boards Cleaned Overnight in Acid



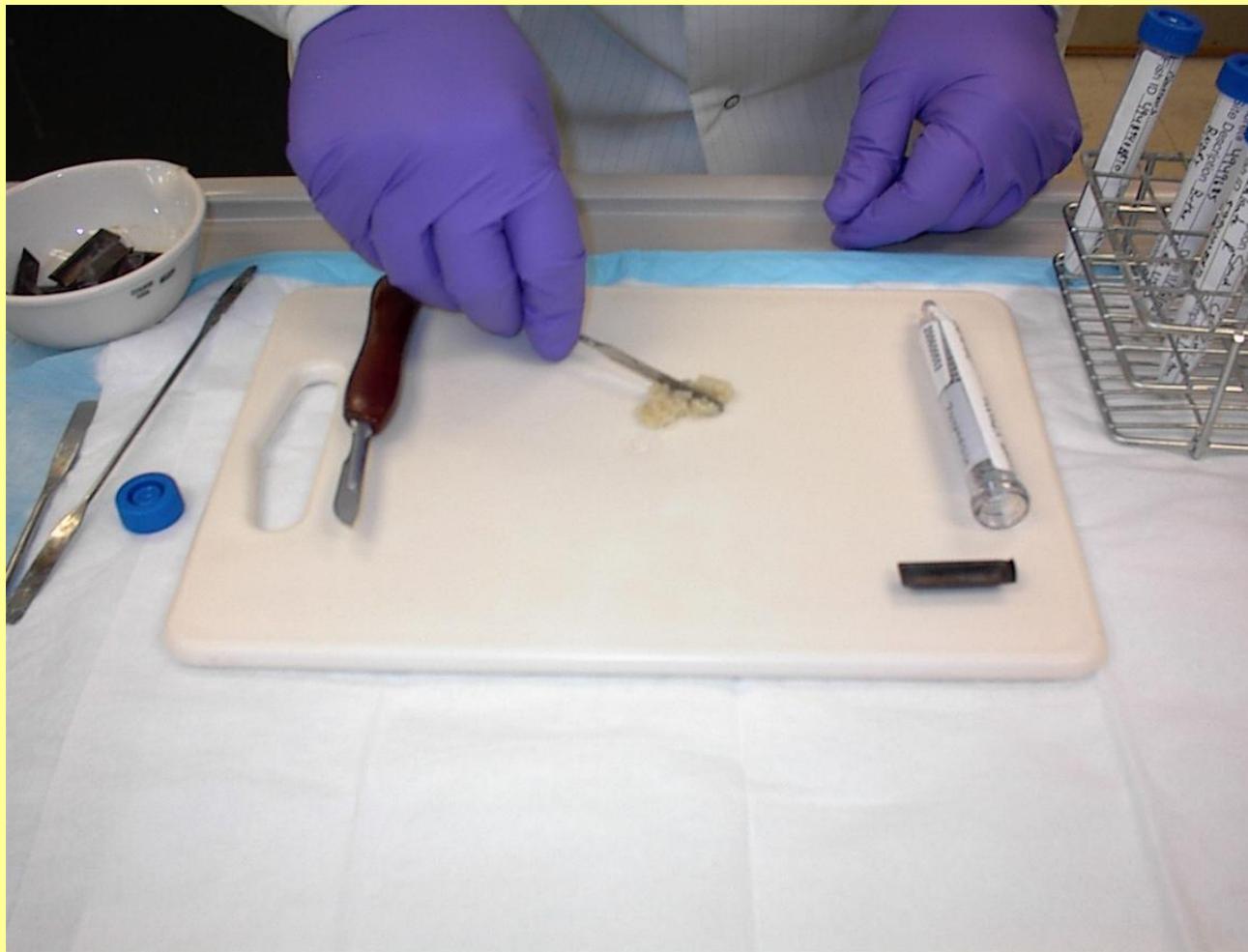
Cutting Boards are also Cleaned with Ultra-Pure Water



Fish Sample being Removed from Storage Tube



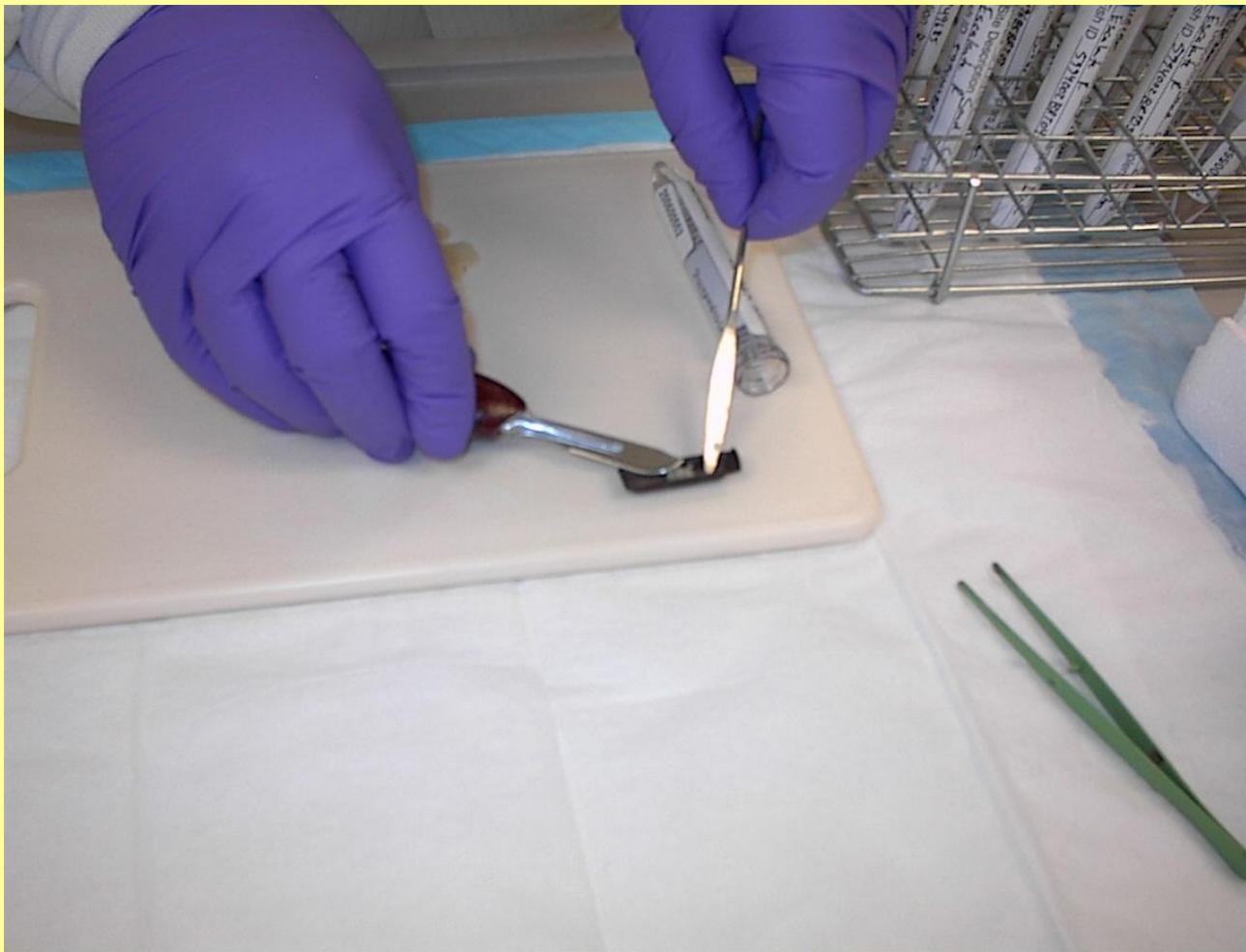
Fish Receiving Additional Homogenization



Fish Sub-Sampling



Fish Sub-Sampling-Loading Nickel Boat



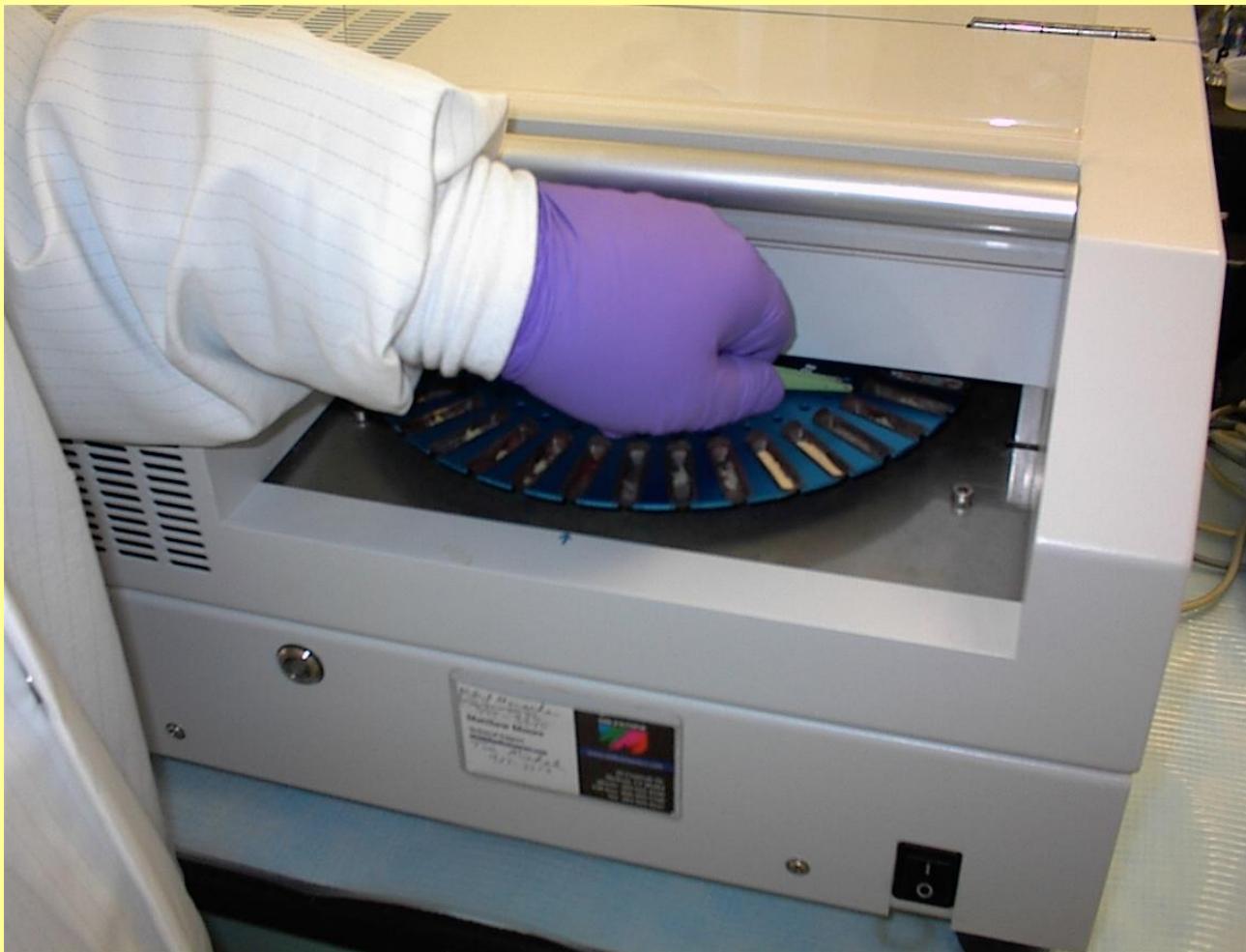
Two are Required for Rapid Work



Mass of Fish Sub-Sample being Determined



Instrument Introduction of Fish Sub-Sample



Instrument Introduction of Water Carryover Sample



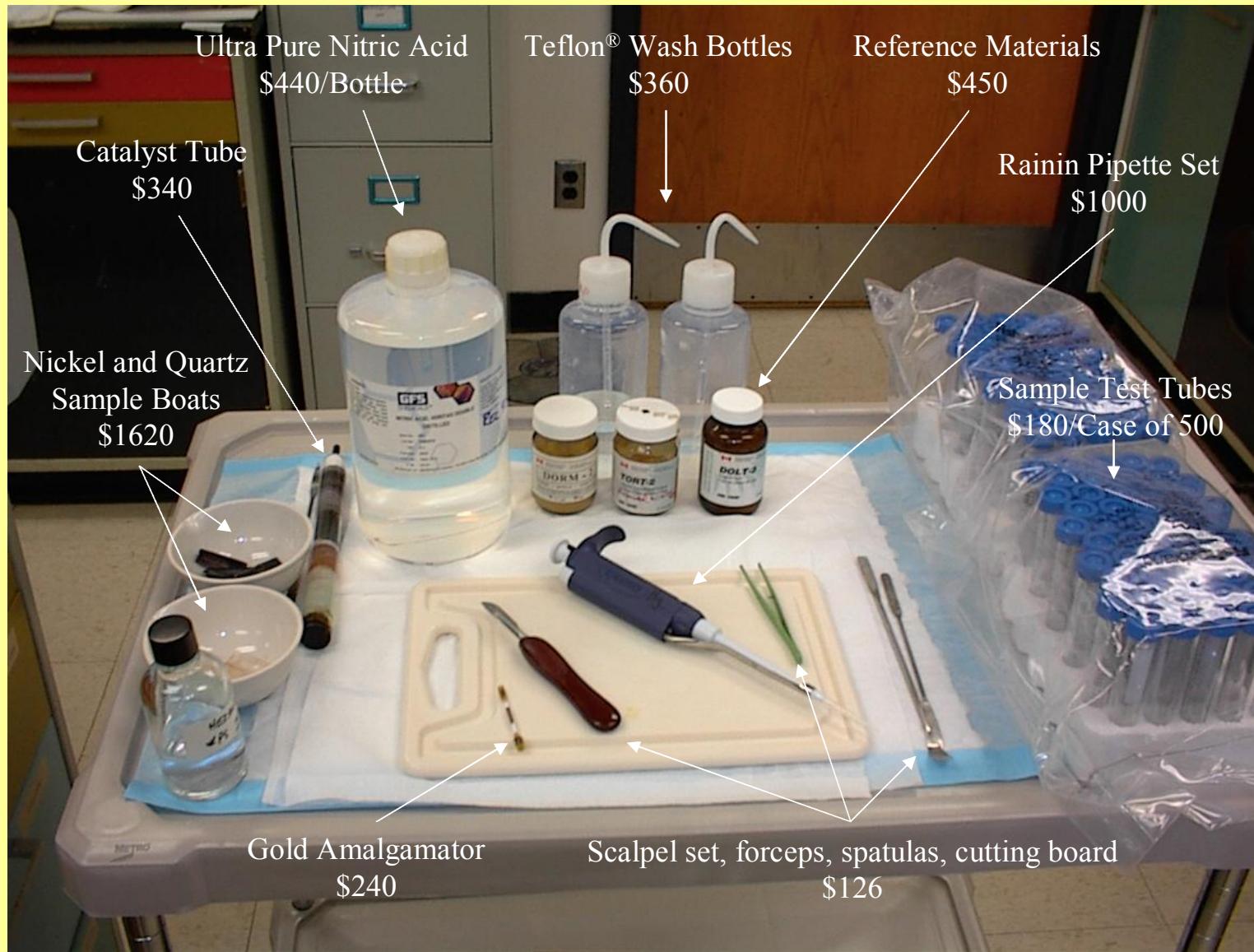
Having Fun Along the Way!



Challenges

- Sample preparation process
- Instrument Down-Time (spent catalyst)
- Instrument Software
- Surge Capacity
- Considerable continuing expenses

Material Costs Incurred by Laboratory



CONCLUSIONS

- Rugged method
- Analysis of plugs resulted in exceeding %RSD criteria
- Homogenizing samples is preferred.
- Over 100 samples analyzed in duplicate.
- Rigorous quality assurance criteria held during all analyses.
- Analytical cost is an ongoing concern.

Questions & Feedback

References

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